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Estefane Isis Teixeira: Investigation, Visualization.

**Cristiane Storck Schwalm**: Investigation, Formal analysis (NMR) and discussion. **Gleison Antônio Casagrande**: Formal analysis (solid state UV-Vis) and discussion.

Bárbara Tirloni: Formal analysis (single crystal X-ray diffraction, Raman), Resources.

Vânia Denise Schwade: Conceptualization, Methodology, Validation, Resources, Writing - Review & Editing.

Johngi



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# Highlights

The isophthaloyl*bis*(*N*,*N*-diphenylthiourea) molecule reacts with metal ions which undergo, in some cases, oxidation or reduction to form stable 2:2 or 2:3 metal to ligand stoichiometric complexes. The transition metal complexes  $[M_2(L-O,S)_2]$  (M = Cu<sup>II</sup> (1), Ni<sup>II</sup> (2)),  $[M_2(L-O,S)_3]$  (M = Fe<sup>III</sup> (4), Co<sup>III</sup> (5)) and  $[Mn_2(L-O,S)_2(dmso)_2]$  (3) were obtained. Complex 3 represents the first manganese complex with thiourea derivative ligand.

# Abstract

The isophthaloyl*bis*(*N*,*N*-diphenylthiourea) molecule (H<sub>2</sub>L ligand) reacts with Cu<sup>I</sup>, Cu<sup>II</sup>, Mn<sup>III</sup>, Fe<sup>II</sup> and Co<sup>II</sup> ions to form binuclear complexes with formula  $[M_2(L-O,S)_2]$  (M = Cu<sup>II</sup> (1), Ni<sup>II</sup> (2)) or  $[M_2(L-O,S)_3]$  (M = Fe<sup>III</sup> (4), Co<sup>III</sup> (5)). In presence of dimethyl sulfoxide,  $[Mn_2(L-O,S)_2(dmso)_2]$  (3) was successfully obtained and represents the first manganese complex with any thiourea derivative ligand. The ligand and the complexes were characterized by spectroscopic techniques and elemental analysis. Complexes 1, 3, 4 and 5 were structurally analyzed by single crystal X-ray diffraction data, confirming the *O*,*S* chelating coordination mode. The stoichiometries were confirmed by thermal analysis with formation of the corresponding metal oxides. The set of the performed analysis corroborated that some metal

ions undergo oxidation or reduction to form stable 2:2 or 2:3 metal to ligand stoichiometric complexes with  $H_2L$ .

Keywords: isophthaloyl*bis*(*N*,*N*-diphenylthiourea), metal complexes, X-ray diffraction, UV-Vis, NMR, Raman.

### 1. Introduction

Thiourea derivatives possess applications in the field of medicine, agriculture and analytical chemistry. These compounds exhibit a range of biological activities and some of them have shown, for example, good results as antitumor agents [1]. Thiourea based fluorescent photoinduced electron transfer (PET) chemosensors containing neutral aromatic thiourea as receptors have been studied [2], as well as colorimetric naked-eye chemosensors involving proton transfer-based thiourea derivatives [3]. The thiourea groups of *bis*(thioureas) were used as sites for anion receptor systems (such as  $F^-$  and  $AcO^-$ ) induced by hydrogen binding interactions of host for high recognition selectivity for guest [4]. Cu<sup>II</sup> and Ni<sup>II</sup> compounds with *bis*(thiourea) derivatives have been screened for their antioxidant and cytotoxic inhibitions [5]. Additionally, thioureas and their metal complexes have been studied concerning corrosion inhibitor potential and catalytic activities [6].

*N*-benzoylthioureas are versatile bidentate ligands in coordination chemistry, chelating metal ions mainly in an *O*,*S* fashion. Symmetrical quadridentate *bis*(*N*-acyl/aroyl-thioureas) are able to chelate two metal ions due to both *N*-acyl/aroylthioureas functions. These organic molecules are known as bipodal derivatives and are also suitable for the synthesis of multinuclear complexes with diverse architectures controlled by their design. Metal ions such as Cu<sup>II</sup> and Ni<sup>II</sup> form stable complexes with *bis*(*N*-aroylthioureas) [7–9], however, to the best of our knowledge, there are no reports of Mn<sup>II</sup> and Co<sup>III</sup> complexes with isophthaloyl*bis*(*N*,*N*-dialkyl/aryl-thioureas) reported in the literature. In this way, this paper reports the structural and additional characterization of a Cu<sup>II</sup> complex (and the formation of an analogous Ni<sup>II</sup> compound), as well as the spectroscopic, thermal and structural characterization of Mn<sup>II</sup>, Fe<sup>III</sup> and Co<sup>III</sup> binuclear complexes with isophthaloyl*bis*(*N*,*N*-diphenylthiourea).

# 2. Materials and methods

2.1. Chemicals and apparatus

All the metal salts for the synthesis of the complexes were used as received from commercial sources. N,N-diphenylamine and isophthaloyl chloride were purchased from Sigma-Aldrich. KSCN was dried in an oven at 80 °C for 2 hours. Acetone was dried with anhydrous CaSO<sub>4</sub> and distilled prior to the use for the synthesis of H<sub>2</sub>L. Cu(PPh<sub>3</sub>)<sub>3</sub>Br was prepared according to the literature [10]. The elemental analyses were performed on a Perkin Elmer 2400 series II Elemental Analyzer. UV-Vis spectra were recorded at  $1 \times 10^{-5}$  mol L<sup>-1</sup> concentration in DMF solution on a BEL photonics UV-M51 spectrophotometer. Solid UV-Vis spectra were obtained on a Perkin-Elmer UV-Vis lambda 650S spectrophotometer. IR spectra (KBr pellets) were recorded on a Jasco FT-IR-4100 spectrophotometer in the 4000–400 cm<sup>-1</sup> range (4 cm<sup>-1</sup> of resolution). Raman spectra were measured on a Bruker SENTERRA Raman Microscope from 3500 to 50 cm<sup>-1</sup>. NMR spectra were recorded on a Bruker DPX-NMR or Avance III spectrometer, operating at 400 or 500 MHz for <sup>1</sup>H nuclei, respectively, using THF- $d_8$  or CDCl<sub>3</sub> as solvents. High-resolution mass spectra for H<sub>2</sub>L was obtained on a Micromass Waters Q-Tof spectrometer (ESI positive mode) in acetonitrile. TG-DSC curves were obtained on a NETZSCH STA 449 F3 thermal analyser using air atmosphere in the range of 30–1000 °C with heating rate of 10 °C min<sup>-1</sup> on an  $\alpha$ -alumina crucible. The single crystal data collection for the complexes was performed on a Bruker D8 Venture Photon 100 diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods, and least-squares refinement of the structures was performed by the SHELXL-2018 program [11]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined isotropically.

# 2.2. Synthesis

# 2.2.1. Synthesis of isophthaloylbis(N,N-diphenylthiourea), H<sub>2</sub>L

The synthesis of  $H_2L$  was done under nitrogen atmosphere according to the literature [1, 12] with some modifications. An acetone solution (30 mL) of isophthaloyl chloride (2.03 g, 0.01 mol) was added dropwise, by using an addition funnel, to an acetone solution (30 mL) of potassium thiocyanate (1.94 g, 0.02 mol). The solution became turbid white. This mixture was stirred for additional 1 h at room temperature. Then, a diphenylamine (3.38 g, 0.02 mol) solution (in 25 mL of acetone) was slowly added using an addition funnel. The mixture turned slightly orange with a clear solid. After heating under reflux and stirring for 30 min, the mixture was cooled to room temperature and then poured on a beaker with cold water in an

ice bath. A gelatinous product formed and the supernatant was removed. To the gelatinous product was added methanol, affording the  $H_2L$  ligand as a yellow solid. In another procedure, solid  $H_2L$  was also obtained by storing the aqueous mixture in the refrigerator for approximately 12 h.

Purification of the crude product was done in column chromatography using ethyl acetate/hexane or chloroform/methanol mixtures as eluents.

### 2.2.2. Synthesis of the metal complexes

 $[Cu_2(L-O,S)_2]$  (1). CuCl<sub>2</sub>·2H<sub>2</sub>O (34 mg, 0.20 mmol) was dissolved in 3 mL of methanol and added to a H<sub>2</sub>L (117 mg, 0.20 mmol) solution in 8 mL of dichloromethane in the presence of 0.30 mL of triethylamine. After 1.5 h under stirring at room temperature, the formed solid was isolated by simple filtration, washed with methanol and dried.

The same product was obtained in a reaction using  $Cu(PPh_3)_3Br$  (0.20 mmol) instead of  $CuCl_2 \cdot 2H_2O$ . In this case, the copper(I) starting material was dissolved in 5 mL of an acetonitrile/dichloromethane mixture (1:1). The clear solution was stored and needle shaped brown crystals of  $[Cu_2(L-O,S)_2] \cdot 2CH_2Cl_2$  were formed within one day.

 $[Ni_2(L-O,S)_2]$  (2). NiCl<sub>2</sub>·6H<sub>2</sub>O (47 mg, 0.20 mmol) was dissolved in 3 mL of methanol and added to a H<sub>2</sub>L (117 mg, 0.20 mmol) solution in 8 mL of dichloromethane containing 0.30 mL of triethylamine. After 1.5 h under stirring at room temperature, the formed solid was filtered, washed with methanol and dried.

 $[Mn_2(L-O,S)_2(dmso)_2]$  (3). Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (80 mg, 0.30 mmol) was dissolved in 2 mL of dimethyl sulfoxide and added to a H<sub>2</sub>L (176 mg, 0.30 mmol) solution in 3.5 mL of dichloromethane with 0.30 mL of triethylamine. After 1.5 h under stirring at room temperature, the solution was filtered and stored. Within 5 days the orange-red block shaped crystals of  $[Mn_2(L-O,S)_2(dmso)_2]$ ·4DMSO·0.5H<sub>2</sub>O were collected.

[Fe<sub>2</sub>(L-O,S)<sub>3</sub>] (4). FeSO<sub>4</sub>·7H<sub>2</sub>O (56 mg, 0.20 mmol) was dissolved in 3 mL of methanol and added to a H<sub>2</sub>L (176 mg, 0.30 mmol) solution in 8 mL of dichloromethane in presence of 0.45 mL of triethylamine. The solution changed to turbid black. After 1.5 h under stirring at room temperature, the formed solid was collected by filtration, washed with methanol and dried.

The same product was also obtained in reaction using  $FeCl_3$  (0.20 mmol) and *N*,*N*-dimethylformamide as solvent.

Recrystallization was performed from dichloromethane solution with slow diffusion of diethyl ether. Within 2 days black plate shaped crystals of  $[Fe_2(L-O,S)_3]\cdot 0.25CH_2Cl_2\cdot 0.35H_2O$  were obtained.

 $[Co_2(L-O,S)_3]$  (5). CoCl<sub>2</sub>·6H<sub>2</sub>O (48 mg, 0.20 mmol) was dissolved in 4 mL of acetonitrile and added to a H<sub>2</sub>L (176 mg, 0.30 mmol) solution in 8 mL of dichloromethane. The solution became green. Then 0.45 mL of triethylamine was added and some green solid started to form. After 1.5 h under stirring at room temperature, the solid was isolated by simple filtration and the solution was left to slow evaporation of the solvents. After 7 days, green needle shaped crystals of  $[Co_2(L-O,S)_3]$ ·6CH<sub>3</sub>CN·0.5CH<sub>2</sub>Cl<sub>2</sub>·0.5H<sub>2</sub>O were observed.

When the same synthesis was carried out replacing acetonitrile by methanol, green plate shaped crystals of  $[Co_2(L-O,S)_3]$ ·4CH<sub>2</sub>Cl<sub>2</sub>·CH<sub>3</sub>OH·4H<sub>2</sub>O were formed in the mother solution. If more methanol (8 mL) was added to the green solution after 1 h of reaction, precipitation of a green solid is observed. The solid was isolated by filtration within 30 min of additional stirring, washed with methanol and dried. In the next day, the additional green solid which deposited in the mother solution was also isolated.

### 3. Results and discussion

3,3,3',3'-tetraphenyl-1,1'-isophthaloyl*bis*(thiourea), namely in this paper isophthaloyl*bis*(*N*,*N*-diphenylthiourea) – H<sub>2</sub>L, can be prepared, as other examples of bipodal 3,3,3',3'-tetraalkyl/aryl-1,1'-aroyl*bis*(thioureas), through the reaction of isophthaloyl chloride and potassium thiocyanate, followed by the addition of the corresponding secondary amine (Scheme 1).



Scheme 1. Synthesis of the H<sub>2</sub>L bipodal ligand.

Isophthaloyl*bis*(*N*,*N*-diphenylthiourea) can be used as a pre-designed chelating ligand to form  $M^{II}$  and  $M^{III}$  complexes *via* self-assembly. Metal to ligand stoichiometries of 2:2 and 2:3 can be achieved, as it has been reported before for  $Cu^{II}$ ,  $In^{III}$ ,  $Fe^{III}$  and some other metal complexes with isophthaloyl*bis*(*N*,*N*-diethylthiourea) [9, 13]. All the complexes (Scheme 2) were obtained in moderate yields and characterized by analytical and spectral techniques. The X-ray crystal structures of compounds [ $Cu_2(L-O,S)_2$ ] (1), [ $Mn_2(L-O,S)_2(dmso)_2$ ] (3), [ $Fe_2(L-O,S)_3$ ] (4) and [ $Co_2(L-O,S)_3$ ] (5) reveal binuclear arrangements. For the [ $Ni_2(L-O,S)_2$ ] (2) compound it is suggested to possess the same structure as 1, which is supported by analytical and spectral data. Compound 2 presented poor solubility in most of the common organic solvents, even in pyridine, when an adduct could be formed [14, 15]. No evidences of adduct formation was observed since the solid maintained its color and did not dissolve even under mild heating. In the literature, related Ni<sup>II</sup> adducts have green color, being the crystals very fragile, disintegrating rapidly on removal from the pyridine mother liquor [14]. Additionally, due to the low solubility, it cannot be ruled out the possibility of a polymeric structure with formula {Ni(L-O,S)}*n*.



Scheme 2. Synthesis of 2:2 and 2:3 self-assembled  $M^{II}$  and  $M^{III}$  complexes. Conditions: r.t., 2 h, Et<sub>3</sub>N as base.

Reactions of isophthaloyl*bis*(*N*,*N*-diphenylthiourea), H<sub>2</sub>L, with metal(II) ions in the presence of triethylamine as base yielded binuclear complexes. Characterization and structure analysis of the complexes were accomplished by elemental analysis, spectroscopic techniques such as IR and Raman, as well as electronic absorption and thermal analysis. The prepared complexes have shown characteristic colors, indicating oxidation of the metal ions in case of using Cu<sup>I</sup>, Fe<sup>II</sup> and Co<sup>II</sup> salts as starting materials, and reduction in case of using Mn<sup>III</sup> salt. Oxidations are attributed to the atmospheric oxygen present during the reaction synthesis. Reduction of Mn<sup>III</sup> to Mn<sup>II</sup> is probably related to the oxidation of some ligand during the reaction to promote the reduction of Mn<sup>III</sup>. The consumption of part of the ligand in the redox reaction led to a lower yield of complex **3**. It is well known that thiourea oxidizes chemically and

electrochemically [16, 17]. In the oxidation, S–S bonds are formed (Eq. 1) which, in this case, can happen between two *bis*(thiourea) molecules or between distinct molecules (Figure 1). Oxidation has been also observed with aroilselenoureas in the formation of benzoylformamidine diselenide [18]. Additionally, manganese (III) acetate is used as an oxidizing agent for many oxidations of organic compounds [19]. Finally, the reaction between  $H_2L \ bis$ (thiourea) and Mn(OAc)<sub>3</sub> represents a clear redox process.

$$2C_{6}H_{4}[C(O)NHC(S)N(C_{6}H_{5})_{2}]_{2} \rightarrow \{C_{6}H_{4}[C(O)N=CN(C_{6}H_{5})_{2}]_{2}S\}_{2} + 4e^{-} + 4H^{+}$$
 Eq. 1



Figure 1. Representation proposal of S–S bonds formation in the oxidation of thiourea.

The complexes are stable at room temperature and have shown hygroscopicity, as can be seen in the elemental analysis results. Table 1 summarizes the important analytical and physical data of the ligand and complexes 1 - 5. The ligand to metal stoichiometries of the complexes are 2:2 or 2:3. In case of complex 3, dimethyl sulfoxide is present as a ligand and as a crystallization solvent in the complex since this compound was obtained only as a crystalline product. In all other complexes, the solvents dichloromethane, acetonitrile or methanol (present in the crystal structures in some cases) are presumably not present in the powder samples due to their volatility.

Comp.Ligand/ComplexNr.M. Formula (F. Wt)		Viold	Elemental analysis, %				
	M Formula (F Wt)	Color	(%)	Found/(Calc.)			
			(70)	С	Н	N	
	H <sub>2</sub> L	Yellow	53	70.01	4.80	8.82	
	$C_{34}H_{26}N_4O_2S_2\ (586.73)$			(69.60)	(4.47)	(9.55)	
1	$[Cu_2(L-O,S)_2]\cdot 2H_2O$	Brown	82	61.45	3.31	8.42	
	$C_{68}H_{52}N_8O_6S_4Cu_2\ (1332.54)$			(61.29)	(3.93)	(8.41)	

Table 1. Analytical and physical data of H<sub>2</sub>L ligand and metal complexes.

2	$[Ni_2(L-O,S)_2] \cdot H_2O$	Light	70	62.72	3.62	8.46
	$C_{68}H_{50}N_8O_5S_4Ni_2\ (1304.82)$	brown		(62.59)	(3.86)	(8.59)
3	$[Mn_2(L-O,S)_2(dmso)_2] \cdot 4DMSO \cdot 0.5H_2O$	Reddish	32	53.33	4.21	6.19
	$C_{80}H_{85}N_8O_{10.5}S_{10}Mn_2\ (1757.10)$	orange		(54.68)	(4.88)	(6.38)
4	$[Fe_2(L-O,S)_3] \cdot 4H_2O$	Black	89	62.52	3.64	8.84
	$C_{102}H_{80}N_{12}O_{10}S_6Fe_2\ (1937.88)$			(63.22)	(4.16)	(8.67)
5	$[\mathrm{Co}_2(\mathrm{L}\text{-}O,S)_3]\cdot 2\mathrm{H}_2\mathrm{O}$	Green	98	64.89	3.91	8.57
	$C_{102}H_{76}N_{12}O_8S_6Co_2\ (1908.03)$			(64.21)	(4.01)	(8.81)

The obtention of the H<sub>2</sub>L bipodal ligand was confirmed by mass spectrometry and by infrared, Raman and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. In the high resolution mass spectrum of the ligand, the  $[M+H]^+$  peak was detected at m/z 587.1945 (calc. 587.1575). The peak at m/z1173.3719 (calc. 1173.3073) refers to a protonated ion cluster,  $[M_2+H]^+$ , indicating that the molecule might exist as a dimer under the ionization conditions. The spectra are given in the Supporting Information (Figures S1–S3). Possible  $\alpha$ –thioamide cleavage occurs under the ionization condition since peaks at m/z 418.0981 (calc. 418.0678) and m/z 212.0777 (calc. 212.0528) are observed.

### NMR spectroscopy

In the <sup>1</sup>H NMR spectra of the ligand (in THF- $d_8$ ), the NH protons are observed as a singlet at 10.19 ppm and the *ortho*-carbonyl hydrogens from the isophtalic spacer are observed as a triplet at 7.93 ppm (1H, J = 1.5 Hz) and a doublet of doublets at 7.72 ppm (2H, J = 7.7 and 1.7 Hz). The signal from the remaining phenylene hydrogen most probably overlaps with the two broad multiplets observed between 7.4–7.1 ppm, which correspond to the remaining twenty hydrogens from the two *N*-diphenyl terminal substituents. These data are presented in Table 2.

The <sup>1</sup>H NMR spectrum of the ligand was also recorded in CDCl<sub>3</sub> in order to allow a straight comparison with a Co<sup>III</sup> complex analyzed in the same solvent. In this case, the NH protons are observed as a broad singlet at 8.84 ppm, while the hydrogens from the spacer appear as singlet at 7.87 ppm (1H), a doublet of doublets at 7.74 ppm (2H, J = 7.8 and 1.6 Hz) and a triplet at 7.41 ppm (1H, J = 7.8 Hz). This latter signal partially overlaps with a multiplet (7.4-7.3 ppm), corresponding to the remaining hydrogens from the two *N*-diphenyl terminal

substituents. The observed chemical shifts compare well with an analogous isophthaloyl*bis*(*N*,*N*-diethylthiourea) derivative [7].

In the <sup>13</sup>C NMR spectra of the same compound (Figure 2), the signals at  $\delta$  185.4 and 163.2 ppm are attributed to the thiocarbonyl and carbonyl groups, respectively. Although there are no <sup>13</sup>C NMR data available in the literature for comparison, all the expected signals related to the aromatic carbons of this ligand were also accounted for and their chemicals shifts are consistent with the proposed structure. An attempted attribution is presented in Table 2.

Table 2. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts for  $H_2L$  and tentative attributions. <sup>1</sup>H NMR chemical shifts for Co<sup>III</sup> complex.



	C chemical shifts for $H_2L$ in THF- $d_8$										
C=S	C=O	Phenylene central ring				Phenyl rings					
(C6)	(C5)	C1	C2	C3 (	24	C7/C7	" C8/C8'	C9/C9'	C10/C10'		
185.4	163.2	128.6	132.5 1	34.8 12	9.2	147.6	129.7 ai	nd 128.2	127.6		
<sup>1</sup> H chemical shifts											
			N_H	Pher	nylene	e central	l ring	Phen	yl rings		
			1, 11	H1	ł	43	H4	(H8-H10	/H8'-H10')		
H <sub>2</sub> L (THF- <i>d</i> <sub>8</sub> ) 10.19 (s) 7.			7.93 (t)	7.72	2 (dd)	7.4 – 7.1	7.4 –	7.1 (m)			
$H_2L$ (CDCl <sub>3</sub> ) 8.84 (s)			7.87 (s)	7.74	(dd)	7.41 (t)	7.4 –	7.3 (m)			
[Co <sub>2</sub> (L-	<i>O</i> , <i>S</i> ) <sub>3</sub> ] (5	( <b>CDCl</b> <sub>3</sub> )	_	9.50 (t)	7.43	8 (dd)	6.89 (t)	7.4 –	7.2 (m)		



Figure 2. <sup>13</sup>C NMR spectrum (100 MHz) of  $H_2L$  in THF- $d_8$ .

The Co<sup>III</sup> ( $d^6$ ) binuclear complex could also be analyzed by NMR spectroscopy due to its diamagnetic low spin character ( $t_{2g}{}^6e_g{}^0$  configuration). Its <sup>1</sup>H NMR spectrum was obtained in CDCl<sub>3</sub> as the solvent (Figure S6), and the absence of the NH resonance signal clearly indicates a complexation reaction involving deprotonation of H<sub>2</sub>L. Further evidence of complex formation are the shifts of the signals related to hydrogens on the isophtalic spacer of the ligand, now observed at  $\delta$  9.50 (t, J = 1.6 Hz), 7.43 (dd, J = 7.7 Hz, J = 1.8 Hz) and 6.89 (t, J = 7.7 Hz) ppm. The upfield for the H4 signal shift (from 7.41 to 6.89 ppm), as well as the remarkable downfield shift for H1 (from 7.87 to 9.50 ppm), follow the same pattern previously described for a binuclear In<sup>III</sup> complex formation with an analogous ligand [9]. The chemical shifts are listed in Table 2.

# Infrared and Raman spectroscopy

Tables 3 and 4 present the significant IR and Raman spectral data of isophthaloyl*bis*(*N*,*N*-diphenylthiourea), H<sub>2</sub>L ligand, and its metal complexes. Figure 3 shows the IR spectra of the ligand and its complexes for comparison. It can be noted that the IR spectra present a small broad band in 3360–3440 cm<sup>-1</sup> region due to the absorbed water molecules (hygroscopic solids). The Raman spectrum of H<sub>2</sub>L can be found in the supplementary material (Figure S4).

H <sub>2</sub> L	v(N-H)	v(C-H)	v(C=O)	v(C=C)	*	v(NCN)	v(C=S)	δ(С-Н)
IR	3166	3061	1699	1590, 1453	1490	1364	1212	1002
Raman	_	3063	1703	1591, 1453	1491	1365	1163	1004

Table 3. Comparison between selected IR and Raman spectral data for  $H_2L$  (cm<sup>-1</sup>).

*v*: stretching vibration;  $\delta$ : bending vibration; \* probably a combination of v(C=C) and other vibrations.

Table 4. Selected IR and Raman spectral data of the metal complexes.

Nr.	Complex		v(C-H)	v(C <b>≔O</b> )	v(C=C)	v(NCO)	v(NCN)	v(NCS)	<b>v(C∷N</b> )	δ(C-H)
								+ v( <b>CC</b> )		
		IR	3061	1505	1586,	1417	1374	1286	1243	1003
1	$[\operatorname{Cu}_2(\operatorname{L-}O,S)_2]$				1489					
		Raman	3072	1505	1587	1446	1382	1299	1268	1002
		IR	3057	1508	1586,	1415	1384	1290	1249	1003
2	$[Ni_2(L-O,S)_2]$		5057		1491					
		Raman	3055	1521	1587	1460	1387	1293	1272	1001
		IR	3059,	1514	1585,	1406	1358	1289	1235	1003
3	$[Mn_2(L-$		2907		1491					
5	$O,S)_2(dmso)_2]$	Raman	3084,	1530	1588	1440	1362	1289	1264	1003
			2887							
		IR	3058	1506	1589,	1422	1381	1285	1244	1003
4	$[Fe_2(L-O,S)_3]$				1489					
		Raman	3057	1524	1593	1454	1394	1293	1266	1003
		IR	3060	1517	1588,	1410	1370	1284	1246	1003
5	$[Co_2(L-O,S)_3]$				1490					
		Raman	3047	1512	1591	1447	1390	1292	1268	1002

*v*: stretching vibration;  $\delta$ : bending vibration.



Figure 3. IR spectra of H<sub>2</sub>L and metal complexes.

In the IR spectrum of H<sub>2</sub>L, the C=O and C=S stretching vibration band appear at 1699 and 1212 cm<sup>-1</sup>, respectively. The N–H stretching band is observed at 3166 cm<sup>-1</sup>. These values are close to those reported earlier for this molecule and analogues [1, 12]. On comparison of the IR spectra of the ligand with its metal complexes, the N–H stretching band disappears and the C=O stretching band shifted from 1699 cm<sup>-1</sup> to around 1510 cm<sup>-1</sup>. This shift of more than 150 cm<sup>-1</sup> to lower frequencies means that with the deprotonation on the –C(S)-NH-C(O)– fragments of the ligand a charge delocalization occurs between the isophthaloyl*bis*(thioureate) anions on coordinating with the metal ions, reflecting the formation of *O*,*S* chelates (Figure 4). The same trend of shifting would be expected for the thiocarbonyl stretching vibration frequencies, however this vibration for the complexes could not be assigned unambiguously since it is located in the fingerprint zone of the IR spectra.



Figure 4. Representation of the deprotonation process with charge delocalization in the chelating rings.

In the Raman spectra, the symmetric and antisymmetric M–O and M–S stretching modes are probably located in the 420–260 cm<sup>-1</sup> range (Figure 5). The exact attribution cannot be done without support of computational studies.



Figure 5. Raman spectra of the complexes in the 900–100 cm<sup>-1</sup> region. The *v*(M–O) and *v*(M–S) bands are probably located in the window highlighted with the blue dashed lines.

### UV-Vis spectroscopy

The electronic absorption spectra of H<sub>2</sub>L was investigated in solution and in solid state (Figure 6). In solution, a thin band at 268 nm and another large band centered at approximately 328 nm could be identified. The band at 268 nm is characteristic for  $\pi \rightarrow \pi^*$  intraligand charge transition (ICT) and its intensity agrees with the presence of several aromatic groups in H<sub>2</sub>L. The band at 328 nm can be attributed to  $n \rightarrow \pi^*$  ICT involving electron pairs of carbonyl and thiocarbonyl groups. In the solid state, there are three bands in the spectrum: at 250, 312 and 375 nm. The bands at 250 and 312 nm should be related to the  $\pi \rightarrow \pi^*$  transitions. For comparison, in solid state, absorption due to  $n \rightarrow \pi^*$  transitions has been observed for terphenyl carboxylic acid derivative at 365 nm [20] and, in case of *bis*(thiosemicarbazones), it has been observed at *ca*. 333 nm [21]. For the *bis*(thiourea) ligand in this work, possible N–H···S hydrogen bonds between *bis*(thiourea) molecules in the solid state might be promoting UV-Vis absorptions at lower energies compared to absorption in solution.



Figure 6. Solid state and DMF solution UV-Vis spectra of H<sub>2</sub>L.

The metal complexes formation was also confirmed by the UV-Vis spectra. In the solid state, ligand to metal charge transitions (LMCT) and *d*-*d* transitions are more easily observed than in diluted solutions. These transitions appear as large bands in the range of 450 to 800 nm of the spectra, as it can be seen in Figure 7. Complexes 1 and 2 have shown bands from 700 to 460 nm, related to d-d electronic transitions, typical for ions in quadratic environment: (v1 =  ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ ), for Cu<sup>II</sup> ( $d^{9}$ ); and (v2 =  ${}^{3}T_{1g}(F) \rightarrow {}^{3}T_{1g}(P)$ ), for Ni<sup>II</sup> ( $d^{8}$ ) [22]. Complexes 4 and 5, which are isostructural species due to their octahedral environments, have shown a broad band centered at 570 nm (complex 4) or 650 nm (complex 5). For the  $Co^{III}$  ( $d^6$ ) complex, also a slight shoulder at 480 nm can be observed, being these bands attributed to the electronic d-dtransitions (v1 =  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  and v2 =  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ ), typical for Co<sup>III</sup> in octahedral environment [23]; while for the Fe<sup>III</sup> ( $d^5$ ) complex, the ( $\nu 1 = {}^2T_{2g} \rightarrow {}^6A_{1g}$ ) electronic transition appears. The same  ${}^{2}T_{2g} \rightarrow {}^{6}A_{1g}$  electronic transition is observed for the isoelectronic Mn<sup>II</sup> ( $d^{5}$ ) complex (complex 3) throughout the band centered at approximately 525 nm. For all the complexes, the highest energy bands (centered approximately at 380 and 250 nm) are related to the LMCT and  $\pi$ - $\pi$ \* electronic transitions (involving aromatic rings of the ligand in the latter case), respectively.



Figure 7. Solid state UV-Vis spectra of the complexes.

In solution, the UV-Vis spectra of the complexes showed a hyperchromic effect when compared with the free ligand. This effect is related to the appearance of new LMCT electronic transitions, which take place after the complexation of the ligands to the metal centers. These bands are centered at approximately 290 nm, except for complex **3**, where this band is not clearly observed, suggesting that de Mn<sup>II</sup> ions hardly alter the electronic properties of the ligand [20]. Indeed, the ICT ( $n \rightarrow \pi^*$ ) and LMCT bands mask the absorptions due to *d*-*d* transitions in diluted solutions [24]. The  $\pi$ - $\pi^*$  band remained unchanged at 267 nm (see Figure S5 in the supplementary material).

# Thermogravimetric analysis

The thermal stability of the complexes was assigned by thermogravimetric analysis. The metal:ligand stoichiometry inspection was done for all the complexes. The TG data for the investigations were collected in the temperature range of 30-1000 °C. Complex **3** was thermally analyzed using the crystals of  $[Mn_2(L-O,S)_2(dmso)_2] \cdot 4DMSO \cdot 0.5H_2O$ . In the TG-DSC curves of complex **3** (Figure 8) it can be noted that there is a significant mass loss below 200 °C (104–167 °C), which can be explained by the loss of the solvate molecules as an endothermic process. This mass loss corresponds to 18.12% (calc. 18.30%). The coordinated dimethyl sulfoxide molecules are probably eliminated in the subsequent mass loss event when the *bis*(thioureate) ligands decomposition starts. At 900 °C, the complete ligands decomposition under oxidative atmosphere (exothermic processes) leads to formation of manganese oxide (MnO) with residue amount of 9.75% (calc. 8.07%).



Figure 8. TG-DSC curves of complex 3 in air atmosphere.

The thermogravimetric analysis for complexes 1, 2, 4 and 5 was performed using the powder samples isolated at the end of the reaction synthesis. By analysis of the TG curves (Figure S7) it can be noted that for the  $[M_2(L-O,S)_2]$  (M = Cu, Ni) and  $[M_2(L-O,S)_3]$  (M = Fe, Co) complexes the decomposition begins up to 150 °C. Mass loss events due to the decomposition of the *bis*(thioureate) ligands were observed under the oxidative atmosphere. A single decomposition step has been observed for complex 2. At 900 °C, the formation of metal oxides MO (M = Cu, Ni) or M<sub>2</sub>O<sub>3</sub> (M = Fe, Co) as residues were evaluated. The residues amounts for MO are 8.54% (calc. 11.61% for 2) and 11.68% (calc. 12.27% for 1) while for M<sub>2</sub>O<sub>3</sub> the amounts are 9.61% (calc. 8.56% for 4) and 11.14% (calc. 8.86% for 5). Complex 2 showed the highest stability (up to 350 °C). This observation probably reflects the

strong interaction of  $Ni^{II}$  ions and the deprotonated thiourea ligands which does not allowed us to proceed recrystallization for its structural analysis since there was no solubility.

### Crystal structures

Compounds 1, 3, 4 and 5 were structurally analyzed by single crystal X-ray diffraction. Table 5 presents the relevant crystallographic data. All complexes have shown binuclear compositions. The structure of 2 is expected to be isostructural to complex 1. The crystallographic data for compound 1 confirms the proposed structure given earlier in the

literature for  $Cu^{II}$  complex with isophthaloyl*bis*(*N*,*N*-diphenylthiourea) [25]. The ellipsoids plots of the structures are available in the supporting information (Figures S8–S12). The X-ray diffraction data for complex **4** were collected at 296 K and the solvents could not be solved in a better way, however it does not gives doubt about the structure of the complex.

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Compound	$[Cu_2(L-O,S)_2] \cdot 2CH_2Cl_2,$	$[Mn_2(L-O,S)_2(dmso)_2]$	$[Fe_2(L-O,S)_3]$	$[Co_2(L-O,S)_3]$	$[Co_2(L-O,S)_3]$
	1	·4DMSO·0.5H <sub>2</sub> O, <b>3</b>	$\cdot 0.25 CH_2 Cl_2 \cdot 0.35 H_2 O, 4$	$\cdot 6CH_3CN \cdot 0.5CH_2Cl_2 \cdot 0.5H_2O$	·4CH <sub>2</sub> Cl <sub>2</sub> ·CH <sub>3</sub> OH·4H <sub>2</sub> O, <b>5</b> '
				, 5	
Molecular formula	$C_{70}H_{52}Cl_4Cu_2N_8O_4S_4$	$C_{80}H_{85}Mn_2N_8O_{10.5}S_{10}$	$C_{102.25}H_{73.20}Cl_{0.50}Fe_2N_{12}O_{6.35}S_6$	$C_{114.5}H_{92}ClCo_2N_{18}O_{6.5}S_6$	$C_{107}H_{92}Cl_8Co_2N_{12}O_{11}S_6$
Formula weight	1466.31	1757.03	1893.31	2169.73	2315.74
Temperature (K)	100(2)	120(2)	296(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	$P2_{1}/n$	<i>P</i> -1	<i>P</i> -1
Unit cell dimensions	a = 9.9410(13)Å	a = 11.8863(5) Å	a = 15.8208(7)  Å	a = 15.4752(8) Å	a = 15.9503(7) Å
	b = 13.548(3) Å	b = 13.0807(5) Å	b = 19.9111(10) Å	b = 17.7934(8) Å	b = 18.1067(9) Å
	c = 13.973(2) Å	c = 15.1958(6) Å	c = 33.1344(17)  Å	c = 21.8201(11) Å	c = 21.7058(10) Å
	$\alpha = 118.607(5)^{\circ}$	$\alpha = 78.8780(10)^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 87.184(2)^{\circ}$	$\alpha = 87.422(2)^{\circ}$
	$\beta = 98.742(4)^{\circ}$	$\beta = 74.0000(10)^{\circ}$	$\beta = 97.701(2)^{\circ}$	$\beta = 85.367(2)^{\circ}$	$\beta = 84.309(2)^{\circ}$
	$\gamma = 94.507(5)^{\circ}$	$\gamma = 66.5560(10)^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 65.716(2)^{\circ}$	$\gamma = 64.2730(10)^{\circ}$
Volume (Å <sup>3</sup> )	1607.9(4)	2074.35(14)	10343.5(9)	5457.9(5)	5619.5(5)
Ζ	1	1	4	2	2
Absorption coefficient	1.015	0.619	0.471	0.507	0.659
$(mm^{-1})$					
F(000)	750	915	3912	2248	2384
Reflections collected /	48927 / 9784 [ <i>R</i> (int) =	66817 / 12692 [R(int) =	616811 / 32157 [ <i>R</i> (int) =	72632 / 33253 [R(int) =	84132 / 18547 [ <i>R</i> (int) =
independent	0.1237]	0.0422]	0.1736]	0.0770]	0.0669]
Data / restraints /	9784 / 0 / 415	12692 / 9 / 530	32157 / 1074 / 1149	33253 / 1 / 1345	18547 / 0 / 1276
parameters					
Goodness-of-fit on $F^2$	1.032	1.032	1.051	1.042	1.029
Final R indices	R1 = 0.0700, wR2 =	R1 = 0.0523, wR2 =	R1 = 0.0994, wR2 = 0.2371	R1 = 0.0836, wR2 = 0.1860	R1 = 0.1032, wR2 = 0.2794
[ <i>I</i> >2sigma( <i>I</i> )]	0.1418	0.1253			
R indices (all data)	R1 = 0.1409, wR2 =	R1 = 0.0749, wR2 =	R1 = 0.1905, wR2 = 0.2826	R1 = 0.1825, wR2 = 0.2197	R1 = 0.1371, wR2 = 0.3060
	0.1611	0.1349			

Table 5. Crystal and structure refinement data for compounds 1, 3, 4 and 5. Crystals of 5 were obtained with different solvate molecules.

The coordination by the *O*,*S* donor atoms is expected in complexes containing deprotonated *bis*(thioureas) working as anionic ligands. The binuclear crystal structures of the Cu<sup>II</sup> (1), Mn<sup>II</sup> (3) and Co<sup>III</sup> (5) complexes are shown in Figures 9–11. For the Fe<sup>III</sup> complex (4), the structure is virtually identical to the Co<sup>III</sup> complex (5) and, for this reason, no additional figures are given for it. Selected bond lengths and angles of complexes 1, 3, 4 and 5 are summarized in Table 6. The corresponding labeling scheme for complex 4 has been adopted from Figure 10a.



Figure 9. (a) Molecular structure of  $[Cu_2(L-O,S)_2] \cdot 2CH_2Cl_2$ , **1**. (b) View along the planar center of the molecule. Hydrogen atoms and solvent molecules were omitted for clarity. Symmetry operator: '-x+1, -y+1, -z+2.



Figure 10. Molecular structure of  $[Mn_2(L-O,S)_2(dmso)_2] \cdot 4DMSO \cdot 0.5H_2O$ , **3**. (b) View along the planar center of the molecule. Hydrogen atoms and solvent molecules were omitted for clarity. Symmetry operator: '-x+1, -y+1, -z+1.



Figure 11. (a) Molecular structure of  $[Co_2(L-O,S)_3] \cdot 4CH_2Cl_2 \cdot CH_3OH \cdot 4H_2O, 5';$  (b) View along the Co–Co connecting direction. Hydrogen atoms and solvent molecules were omitted for clarity.

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Bond	$[Cu_2(L-O,S)_2]$	$[Mn_2(L-O,S)_2(dmso)_2]$	Bond	$[Fe_2(L-O,S)_3]$	$[Co_2(L-O,S)_3]$	$[Co_2(L-O,S)_3]$
(M = Cu  or  Mn)	$\cdot 2CH_2Cl_2, 1$	·4DMSO·0.5H <sub>2</sub> O, <b>3</b>	(M = Fe  or  Co)	·0.25CH <sub>2</sub> Cl <sub>2</sub> ·0.35H <sub>2</sub> O, <b>4</b>	·6CH <sub>3</sub> CN·0.5CH <sub>2</sub> Cl <sub>2</sub> ·0.5H <sub>2</sub> O, <b>5</b>	·4CH <sub>2</sub> Cl <sub>2</sub> ·CH <sub>3</sub> OH·4H <sub>2</sub> O, <b>5</b> '
M(1)-S(1)	2.2414(10)	2.5243(6)	M(1)-S(1)	2.4042(13)	2.2150(10)	2.2196(19)
M(1)-S(2)'	2.2513(10)	2.4924(6)	M(1)-S(3)	2.4371(12)	2.2315(12)	2.2185(19)
			M(1)-S(5)	2.4229(13)	2.2500(11)	2.208(2)
			M(2)-S(2)	2.4655(12)	2.2205(10)	2.214(2)
			M(2)-S(4)	2.4347(13)	2.2041(10)	2.247(2)
			M(2)-S(6)	2.4093(12)	2.2153(10)	2.221(2)
	1.005(0)	<b>2</b> 000 ( (1 1)			1.001(0)	1.000(5)
M(1)-O(1)	1.937(2)	2.0804(14)	M(1)-O(1)	2.004(3)	1.931(3)	1.932(5)
$M(1)-O(2)^{\prime}$	1.944(2)	2.0758(15)	M(1)-O(3)	2.006(3)	1.939(2)	1.914(5)
M(1)-O(3)		2.0694(16)	M(1)-O(5)	1.978(3)	1.913(2)	1.942(5)
			M(2)-O(2)	2.038(3)	1.935(2)	1.922(5)
			M(2)-O(4)	1.993(3)	1.942(2)	1.913(5)
			M(2)-O(6)	1.993(3)	1.906(2)	1.930(5)
S(1)-C(13A)	1.728(4)	1.712(2)	S(1)-C(13A)	1.720(4)	1.727(4)	1.735(7)
S(2)-C(14A)	1.725(4)	1.714(2)	S(2)-C(14A)	1.723(4)	1.733(4)	1.726(8)
			S(3)-C(23A)	1.727(5)	1.732(4)	1.732(7)
			S(4)-C(24A)	1.701(5)	1.728(4)	1.755(9)
			S(5)-C(33A)	1.737(5)	1.740(4)	1.729(7)
			S(6)-C(34A)	1.731(5)	1.721(4)	1.723(8)
O(1) C(11A)	1 267(4)	1 261(2)	O(1) C(11A)	1 257(5)	1 257(4)	1 273(8)
O(1)-C(11A)	1.207(4) 1.267(4)	1.201(2) 1.250(2)	O(1)- $C(11A)O(2)$ $C(12A)$	1.237(3) 1.252(5)	1.257(4) 1.254(4)	1.273(8) 1.247(0)
O(2)- $C(12A)$	1.207(4)	1.239(2)	O(2)- $C(12A)$	1.253(5)	1.254(4)	1.247(9) 1.252(0)
			O(3) - C(21A)	1.232(3) 1.258(5)	1.237(3) 1 258(4)	1.232(7) 1.256(0)
			O(4) - C(22A) O(5) C(31A)	1.230(3) 1.254(5)	1.230(4) 1.263(4)	1.250(9) 1.274(8)
			O(5) - C(31A)	1.234(3) 1.264(5)	1.203(4)	1.274(0) 1.269(9)
			O(0) - C(32A)	1.204(3)	1.207(4)	1.208(8)

Table 6. Selected bond lengths (Å) in compounds 1, 3, 4 and 5.

Symmetry operation used to generate equivalent atoms:  $(-x+1, -y+1, -z+2, \text{ for } \mathbf{1}); [-x+1, -y+1, -z+1, \text{ for } \mathbf{3}].$ 

The analysis of the crystal structures shows that the isophthaloylbis(N,N-diphenylthioreate) anions coordinate to a two distinct metal ions since the molecule possesses two arms with oxygen and sulfur donor atoms. The structures of complexes [Cu<sub>2</sub>(L-O,S)<sub>2</sub>] (**1**) and [Mn<sub>2</sub>(L-O,S)<sub>2</sub>(dmso)<sub>2</sub>] (**3**) represent the stable planar arrangement due to the coordination of the bis(thiourea) ligands to the M<sup>II</sup> metal ions. In the other hand, by having a look to the structures of complexes [Fe<sub>2</sub>(L-O,S)<sub>3</sub>] (**4**) and [Co<sub>2</sub>(L-O,S)<sub>3</sub>] (**5**) it can be noted that there is also possible to accommodate three bis(thiourea) ligands in the formation of binuclear complexes, which reflects the flexibility of the chelate system to provide stable coordination environment for M<sup>III</sup> ions.

By means of the C–O distances (that are in the range of 1.25–1.27 Å) and C–S distances (in the range of 1.70–1.75 Å) it is clear that for all the complexes a charge delocalization occurs due to the deprotonation with elongation of the C–O and C–S bonds. For comparison, in free isophthaloyl*bis*(thioureas), these distances are in the range of 1.21–1.23 Å and 1.66–1.68 Å, respectively [12, 14, 15, 26, 27]. The charge delocalization in the –S-C-N-C-O– fragments consequently causes the shortening of the N–C bond lengths in the chelating rings (Figure 4).

The M–O and M–S bond lengths in complexes  $[Cu_2(L-O,S)_2]$  (1) and  $[Fe_2(L-O,S)_3]$  (4) are in accordance with other reported binuclear Cu<sup>II</sup> and Fe<sup>III</sup> complexes with isophthaloyl*bis*(thioureates). In complex 1 the Cu–O and Cu–S distances are 1.937(2)–1.944(2) and 2.2414(10)–2.2513(10) Å, respectively. These distances in Cu<sup>II</sup> complexes in the literature are in the range of 1.93–1.97 Å (Cu–O) and 2.23–2.27 Å (Cu–S) [8, 9, 12]. The geometry of the four-coordinated copper centers is distorted quadratic (Figure 9). In complex 4 the Fe–O and Fe–S distances are in the range of 1.978(3)–2.038(3) and 2.4042(13)–2.4655(12) Å, respectively. The distances in a Fe<sup>III</sup> complex in the literature are in the range of 1.98–2.01 Å (Fe–O) and 2.42–2.46 Å (Fe–S) [13]. The geometry of the six-coordinated iron centers is octahedral.

In complex  $[Co_2(L-O,S)_3]$  (5) the Co–O and Co–S distances are in the range of 1.91–1.94 and 2.20– 2.25 Å, respectively. As expected, these distances are shorter than the distances reported for a binuclear Co<sup>II</sup> complex with isophthaloyl*bis*(*N*,*N*-diisobutylthioureate) (which distances are in the range of 2.00–2.08 Å and 2.30–2.42 Å, respectively) [27]. Co<sup>III</sup> is a smaller ion compared to Co<sup>II</sup> ion having shorter bond lengths with the ligands. This fact is related to the larger attraction of the electrons from the donor atoms of the ligands with the increase of the oxidation state [28]. The geometry of the six-coordinated cobalt centers is octahedral (Figure 11).

The  $Mn^{II}$  complex,  $[Mn_2(L-O,S)_2(dmso)_2]$  (**3**), is the first manganese complex with isophthaloil*bis*(thioureas). It can be found only a trinuclear polymeric compound of  $Mn^{II}Ba^{II}Mn^{II}$  composition with 2,6-dipicolinoyl*bis*(*N*,*N*-morpholinoylthiourea) [29]. In this trinuclear compound (Figure 12),  $Mn^{II}$  occupies the 'side positions', coordinating each one by three sets of *O*,*S* donor

atoms in an octahedral environment. The Ba<sup>II</sup> ions adopt a methanol ligand and each second of them establishes two additional bonds to the adjacent sub-units via a morpholinyl residue, resulting in an infinite *zigzag* chain. In complex **3** obtained in this work (Figure 10), chelating coordinating mode by *O*,*S* donor atoms was also observed with Mn<sup>II</sup> ions. However, the Mn–O and Mn–S distances in complex **3** (2.0758(15)–2.0804(14) and 2.4924(6)–2.5243(6) Å, respectively) are shorter than those in the trinuclear bimetallic complex (average of 2.17 and 2.57 Å for Mn–O and Mn–S, respectively). This observation can be rationalized by the absence of a big metal ion in the central cavity of the molecule that does not causes elongation especially of the Mn–O bond. The geometry of the five-coordinated Mn<sup>II</sup> ions in complex **3** is pyramidal quadratic (Figure 10). The  $\tau_5$  parameter [30] is equal to 0.19. The apical position is occupied by the oxygen atom of the dimethyl sulfoxide molecule with a bond length of 2.0694(16) Å.



Figure 12. Chain-structure of [BaMn<sub>2</sub>(L)<sub>3</sub>(MeOH)]n [28].

In the crystal structure of complex **3** hydrogen bonds are observed between the water and dimethyl sulfoxide solvate molecules. The distances between the donor and acceptor atoms of the O–H…O hydrogen bonds are 2.800(11) and 2.761(16) Å (Table 7). Hydrogen bonds are also observed between the solvate molecules in the crystal structure of complex **5** which crystallized in a dichloromethane/methanol/water mixture. Details of the O–H…O and O–H…Cl hydrogen bonds are listed in Table 7. Figures S12 and S13 depict those hydrogen bonds.

Table 7. Hydrogen bonds for complexes 3 and 5' [Å and °].

D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)	
$[Mn_2(L-O.S)_2(dms_0)_2] \cdot 4$	DMSO-0.5H <sub>2</sub> O (3)				

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O(3S)-H(1S)O(2S^a)''	0.85(2)	2.33(14)	2.800(11)	115(12)				
O(3S)-H(1S)O(2B^b)''	0.85(2)	2.14(12)	2.761(16)	130(13)				
$[Co_2(L-O,S)_3] \cdot 4CH_2Cl_2 \cdot CH_3O]$	$\frac{1}{[Co_2(L-O,S)_3]\cdot 4CH_2Cl_2\cdot CH_3OH\cdot 4H_2O(5')}$							
O(1S)-H(1SA)O(2S)	0.84	1.87	2.67(2)	160.2				
O(2S)-H(1S)O(1S)	0.88	1.95	2.67(2)	139.0				
O(2S)-H(2S)Cl(6A^a)	0.94	1.92	2.846(19)	166.9				
O(5S^b)-H(7S^b)Cl(8)'	0.85	2.84	3.62(4)	153.5				
O(6S)-H(9S)O(5S^b)	0.85	2.38	3.16(5)	153.8				

Symmetry transformations used to generate equivalent atoms:

For (**3**): '' –*x*+1, –*y*+2, –*z*+2; for (**5**'): ' *x*–1, *y*+1, *z*.

# 4. Conclusion

In this work we demonstrated that isophthaloyl*bis*(*N*,*N*-diphenylthiourea) reacts with first row transition metal ions in the presence of triethylamine as base to generate binuclear complexes with formula  $[M_2(L-O,S)_2]$  ( $M = Cu^{II}(1)$ , Ni<sup>II</sup>(2)) or  $[M_2(L-O,S)_3]$  ( $M = Fe^{III}(4)$ , Co<sup>III</sup>(5)). Oxidation of Cu<sup>I</sup>, Fe<sup>II</sup> and Co<sup>II</sup> ions was observed in reaction with isophthaloyl*bis*(*N*,*N*-diphenylthiourea), as well as reduction of Mn<sup>III</sup> ions in the formation of  $[Mn_2(L-O,S)_2(dmso)_2]$  (3). The complexes were successfully characterized by spectroscopic techniques (IR, Raman, UV-Vis), elemental and thermogravimetric analysis. Co<sup>III</sup> complex (5) was also analyzed by <sup>1</sup>H NMR spectroscopy. Single crystal X ray diffraction data confirmed that the ligand coordinates by the *O*,*S* donor atoms under deprotonation and, more significantly, that it is possible to obtain Mn<sup>II</sup> complexes with thiourea ligands, being complex 3 the first reported example of a non-bimetallic compound.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/xxx. CCDC 1961619, 1961620, 1961621, 1961622 and 1961623 contain the supplementary crystallographic data for this

paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, via www.ccdc.cam.ac.uk/structures.

### References

[1] M. Jamil, M. Zubair, N. Rasool, A.A. Altaf, K. Rizwan, S. Hafeez, I.H. Bukhari, P. Langer, Synthesis, Characterization, Antibacterial and Urease Inhibition Studies of Some Novel Symmetrical N<sup>3</sup>, N<sup>3'</sup>-*bis*-(disubstituted)isophthalyl-*bis*-(thioureas), Asian J. Chem. 25 (10) (2013), 5328–5332.

[2] T. Gunnlaugsson, A.P. Davis, J.E. O'Brien, M. Glynn, Synthesis and photophysical evaluation of charge neutral thiourea or urea based fluorescent PET sensors for bis-carboxylates and pyrophosphate, Org. Biomol. Chem. 3 (2005) 48–56.

[3] C.B. da Silva, T. Kroetz, F.S. Santos, F.S. Rodembuch, Synthesis and Photophysical Characterization of Proton Transfer-Based Thiourea Derivatives: Potential Application as Colorimetric Naked-Eye Chemosensor for Fluoride Detection in Solution, J. Braz. Chem. Soc. 28
(9) (2017) 1830–1841.

[4] T.-B. Wei, W. Wei, C. Cao, Y.-M. Zhang, Synthesis and Anion Recognition of Molecular Tweezers Receptors Based on Acyl-Thiourea, Phosphorus Sulfur, 183 (2008) 1218–1228.

[5] M. Jamil, M. Zubair, M.A. Farid, A.A. Altaf, N. Rasool, F. Nasim, M. Ashraf, M.A. Rashid, S.A. Ejaz, A. Yaqoob, V. U. Ahmad, Study of Antioxidant, Cytotoxic, and Enzyme Inhibition Activities of Some Symmetrical N<sup>3</sup>,N<sup>3'</sup>-Bis(disubstituted)isophthalyl-bis(thioureas) and N<sup>3</sup>,N<sup>3'</sup>,N<sup>3'</sup>,N<sup>3'</sup>-Tetrakis(disubstituted)isophthalyl-bis(thioureas) and Their Cu(II) and Ni(II) Complexes, J. Chem. Soc. Pak. 36(3) (2014) 491–497.

[6] R.K. Mohapatra, P.K. Das, M.K. Pradhan, M.M. El-Ajaily, D. Das, H.F. Salem, U. Mahanta, G. Badhei, P.K. Parhi, A.A. Maihub, M.K. E-Zahan, Recent Advances in Urea and Thiourea-Based Metal Complexes: Biological, Sensor, Optical, and Corrosion Inhibition Studies, Comment Inorg. Chem. 0 (2019) 1–61.

[7] O. Hallale, S.A. Bourne, K.R. Koch, Metallamacrocyclic complexes of Ni(II) with 3,3,3',3'tetraalkyl-1,1'-aroylbis(thioureas): crystal and molecular structures of a 2 : 2 metallamacrocycle and a pyridine adduct of the analogous 3 : 3 complex, Cryst. Eng. Comm. 7(25) (2005) 161–166.

[8] A. Rodenstein, J. Griebel, R. Richter, R. Kirmse, Synthesis, Structure and EPR Investigations of binuclear Bis(N,N,N''',N'''-tetraisobutyl-N,N''-isophthaloylbis(thioureato)) Complexes of Cu<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Pd<sup>II</sup>, Z. Anorg. Allg. Chem. 634(5) (2008) 867–874.

[9] V.D. Schwade, L. Kirsten, A. Hagenbach, E.S. Lang, U. Abram, Indium(III), lead(II), gold(I) and copper(II) Complexes with Isophthaloyl*bis*(thiourea) Ligands, Polyhedron, 55 (2013) 155–161.

[10] B.F. Jardine, L. Rule, A.G. Vohra, The Chemistry of Copper(I) Complexes. Part I: Halogenocomplexes, J. Chem. Soc. (A): Inorg. Phys. Theor. (1970) 238–240.

[11] G. Sheldrick, SHELXTL Version 2018/3, Program for Crystal Structure Refinement, University of Göttingen, 2018.

[12] N. Selvakumaran, N.S.P. Bhuvanesh, R. Karvembu, Self-assembled Cu(II) and Ni(II) metallamacrocycles formed from 3,3,3',3'-tetrabenzyl-1,1'-aroylbis(thiourea) ligands: DNA and protein binding studies, and cytotoxicity of trinuclear complexes, Dalton Trans. 43 (2014) 16395–16410.

[13] C.T. Pham, H.H. Nguyen, A. Hagenbach, U. Abram, Iron(III) Metallacryptand and Metallacryptate Assemblies Derived from Aroyl*bis*(*N*,*N*-diethylthioureas), Inorg. Chem. 56(18)
(2017) 11406–11416.

[14] K.R. Koch, O. Hallale, S.A. Bourne, J. Miller, J. Bacsa, Self-assembly of 2:2 metallomacrocyclic complexes of Ni<sup>II</sup> and Pd<sup>II</sup> with 3,3,3',3'-tetraalkyl-1,1'- isophthaloylbis(thioureas). Crystal and molecular structures of cis-[Pd(L<sup>2</sup>-S,O)]<sub>2</sub> and the adducts of the corresponding Ni<sup>II</sup> complexes: [Ni(L<sup>1</sup>-S,O)(pyridine)<sub>2</sub>]<sub>2</sub> and [Ni(L<sup>1</sup>-S,O)(4-dimethylaminopyridine)<sub>2</sub>]<sub>2</sub>, J. Mol. Struct. 561 (2001) 185–196.

[15] S.A. Bourne, O. Hallale, K.R. Koch, Hydrogen-Bonding Networks in a Bipodal Acyl-thiourea and Its Ni<sup>II</sup> 2:2 Metallamacrocyclic Complex, Cryst. Growth Des. 5(1) (2005) 307–312.

[16] A.E. Bolzán, J.A. Guida, R.C.V. Piatti, A.J. Arvia, O.E. Piro, J.R. Sabino, E.E. Castellano, Formation of *N*,*N*,*N*',*N*'-tetramethylformamidinium disulphide from the chemical and electrochemical oxidation of tetramethylthiourea: Vibrational spectra and crystal structure of the chloride dihydrate salt, J. Mol. Struct. 871 (2007) 131–139.

[17] S. Sahu, P.R. Sahoo, S. Patel, B.K. Mishra, Oxidation of thiourea and substituted thioureas: a review, J. Sulfur Chem. 32(2) (2011) 171–197.

[18] V.D. Schwade, A. Hagenbach, E.S. Lang, K. Klauke, F. Mohr, U. Abram, Oxidorhenium(V)Complexes with Benzoylselenoureas, Eur. J. Inorg. Chem. (2014) 1949–1954.

[19] B.B. Snider, Mechanisms of Mn(OAc)<sub>3</sub>-based oxidative free-radical additions and cyclizations, Tetrahedron, 65(52) (2009) 10735–10744.

[20] L. Fan, X. Zhang, W. Zhang, Y. Ding, W. Fan, L. Sun, Y. Pang, X. Zhao, Syntheses, crystal structures and UV-visible absorption properties of five metal–organic frameworks constructed from terphenyl2,5,2',5'-tetracarboxylic acid and bis(imidazole) bridging ligands, Dalton Trans. 43 (2014) 6701–6710.

[21] C.A. Brown, D.S. West, 2,6-Diacetyl- and 2,6-diformylpyridine *bis*(N4-substituted thiosemicarbazones) and their copper(II) and nickel(II) complexes, Transit. Metal Chem. 28(2) (2003) 154–159.

[22] G.L. Miessler, D.A. Tarr, *Inorganic Chemistry*, 3<sup>rd</sup> Ed., Pearson Prentice Hall, Inc. New Jersey, 2004.

[23] S.S. Tan, A.A. Al-abbasi, M.I.M. Tahir, M.B. Kassim, Synthesis, structure and spectroscopic properties of cobalt(III) complexes with 1-benzoyl-(3,3-disubstituted)thiourea, Polyhedron, 68 (2014) 287–294.

[24] L.A. Saghatforoush, S. Hosseinpour, M.W. Bezpalko, W.S. Kassel, X-ray crystal structural and spectral studies of copper(II) and nickel(II) complexes of functionalized bis(thiosemicarbazone)

ligands and investigation of their electrochemical behavior, Inorg. Chim. Acta, 484(1) (2019) 527–534.

[25] M. Jamil, M. Zubair, A.A. Altaf, M.A. Farid, M.T. Hussain, N. Rasool, I.H. Buchari, V.U. Ahmad, Synthesis, Characterization and Antibacterial Activity of Some Novel Symmetrical N<sup>3</sup>,N<sup>3'</sup>-Bis(disubstituted)isophthalyl-bis(thioureas) and N<sup>3</sup>,N<sup>3</sup>,N<sup>3'</sup>,N<sup>3'</sup>-Tetrakis(disubstituted)isophthalyl-bis(thioureas) and Their Cu(II) and Ni(II) Complexes, J. Chem. Soc. Pak. 35(3) (2013) 737–743.

[26] N. Selvakumaran, R. Karvembu, S.W. Ng, E.R.T. Tiekink, 1-[3-({[Bis(2-methylpropyl)carbamothioyl]amino}carbonyl)benzoyl]-3,3-bis-(2-methylpropyl)thiourea, Acta Cryst. (2013) E69, o1368.

[27] A. Rodenstein, R. Richter, R. Kirmse, Synthesis and Structure of N,N,N<sup>'''</sup>,N<sup>'''</sup>-Tetraisobutyl-N',N<sup>''</sup>-isophthaloylbis(thiourea) and Dimethanol-bis(N,N,N<sup>'''</sup>,N<sup>'''</sup>-tetraisobutyl-N',N<sup>''</sup>-isophthaloylbis(thioureato))dicobalt(II), Z. Anorg. Allg. Chem. 633(10) (2007) 1713–1717.

[28] C.G. Oliveira, P.I. da S. Maia, M. Miyata, F.R. Pavan, C.Q.F. Leite, E.T. de Almeida, V.M. Deflon, Cobalt(III) Complexes with Thiosemicarbazones as Potential anti-*Mycobacterium tuberculosis* Agents, J. Braz. Chem. Soc. 25(10 (2014) 1848–1856.

[29] H.H. Nguyen, J.J. Jegathesh, A. Takiden, D. Hauenstein, C.T. Pham, C.D. Le, U. Abram, 2,6-Dipicolinoylbis(N,N-dialkylthioureas) as versatile building blocks for oligo- and polynuclear architectures, Dalton Trans. 45 (2016) 10771–10779.

[30] A.W. Addison, T.N. Rao, Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen–Sulphur Donor Ligands ; the Crystal and Molecular Structure of Aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(ii) Perchlorate, J. Chem. Soc. Dalton Trans. 7 (1984) 1349–1356.



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# Highlights

- 2:2 or 2:3 binuclear complexes formation by oxidation or reduction of metal ions. •
- First example of manganese binuclear complex with thiourea derivative ligand. •
- Spectroscopic, thermal and structural studies on binuclear thioureate compounds. •
- Flexibility of the chelate systems to provide stable coordination environments. •